The Spectroscopic Signature of Aging in δ-Pu

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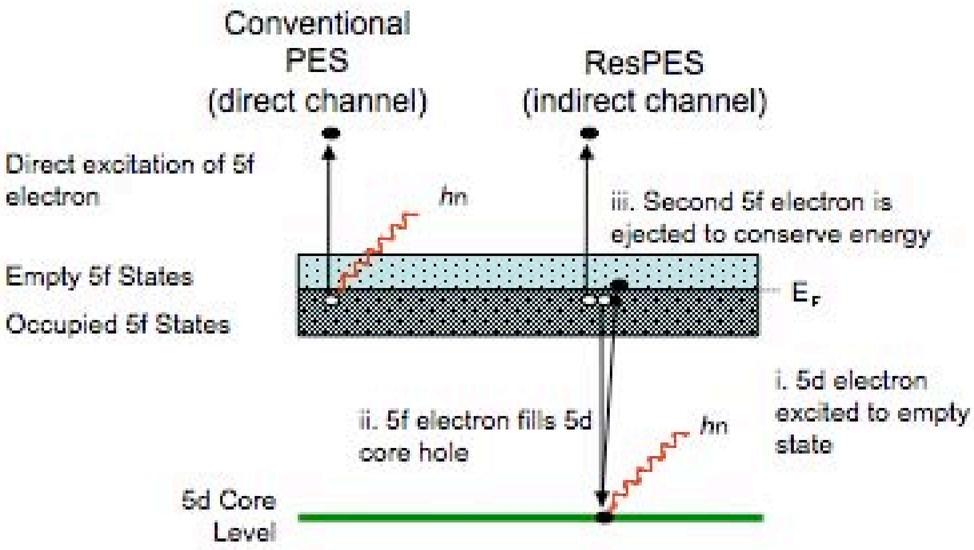
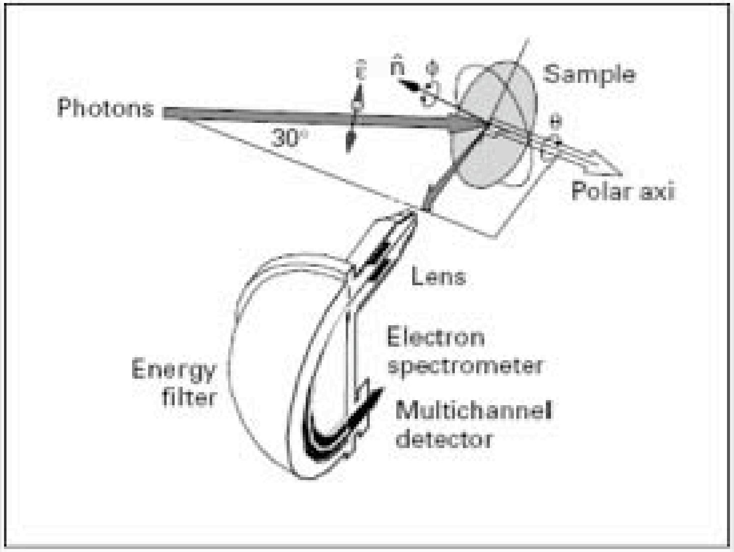
Key references and Collaborators

1. B.W. Chung, A.J. Schwartz, B.B. Ebbinghaus, M.J. Fluss, J.J. Haslam, K.J.M. Blobaum, and J.G. Tobin, "Spectroscopic Signature of Aging in δ-Pu(Ga)," J. Phys. Soc. Japan **75**, No. 5, 054710 (2005).
2. J.G. Tobin, B.W. Chung, R. K. Schulze, J. Terry, J. D. Farr, D. K. Shuh, K. Heinzelman, E. Rotenberg, G.D. Waddill, and G. Van der Laan, "Resonant Photoemission in f-electron Systems: Pu and Gd", Phys. Rev. B **68**, 155109 (2003).
3. J.G. Tobin, S.W. Yu, B.W. Chung, G.D. Waddill, and A.L. Kutepov, "Soft X-ray Studies of Pu Electronic Structure: Past Lessons and Future Directions with BIS," Proceedings of the XAS Actinides Meeting, St. Aubin, France, July 2008, OECD Nuclear Energy Agency (NEA, France).

US/Russian Material Science Workshop, Prague, CR, Aug 30-Sept 4, 2009

One way to interrogate the unoccupied 5f states : RESPES





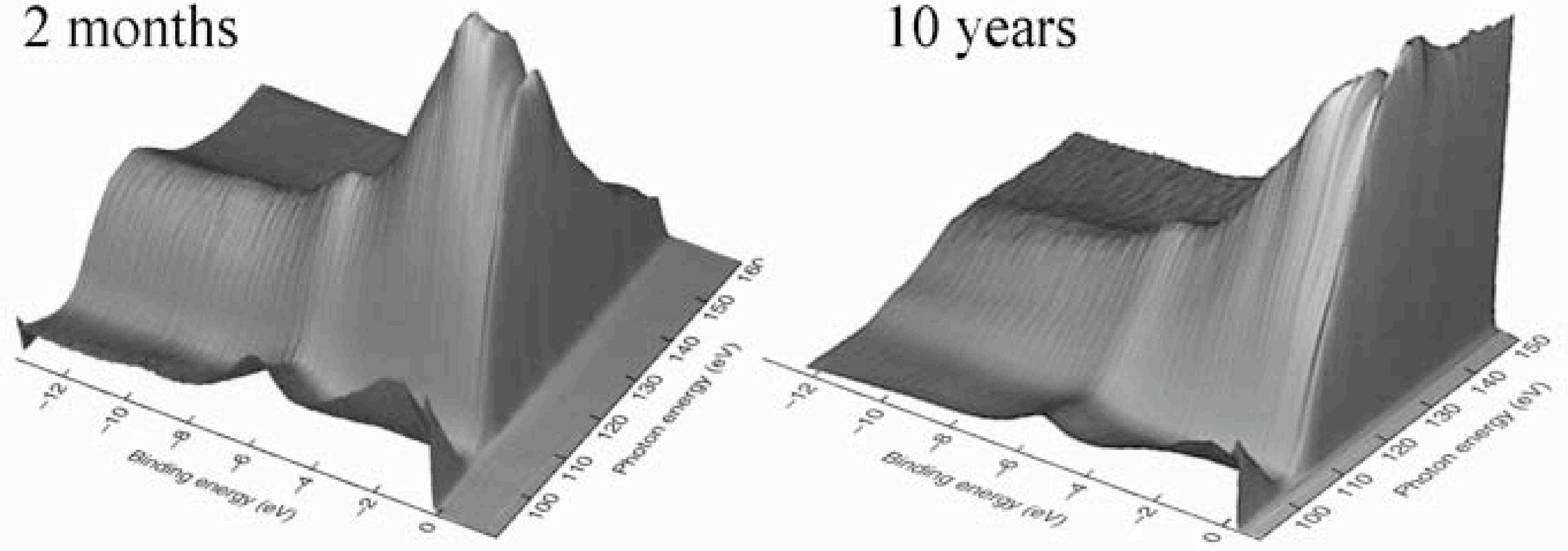
- **Schematic of Conventional and Resonant Photoemission (above).**
- **The direct and indirect excitation channels can interfere destructively (anti-resonance) or constructively (resonance) as the photon energy is tuned through the 5d core level absorption edge, which is about 120 eV for Pu.**

UltraESCA end station at beam line 7.0.1 of the Advanced Light Source.

Resonant photoelectron spectroscopy (RESPES) of Pu shows strong age-dependent effects…but why?

young δ-Pu(Ga)
2 months

aged δ-Pu(Ga)
10 years

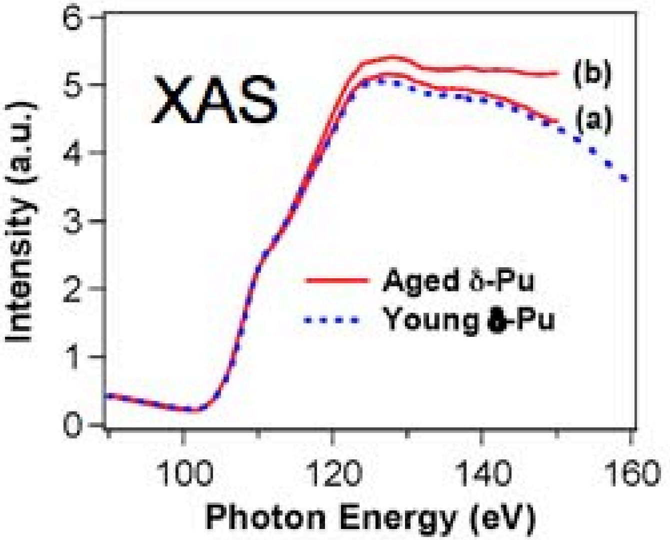


The RESPES spectra for the aged δ-Pu(Ga) exhibit a greater resonant enhancement than those of the young δ-Pu(Ga).

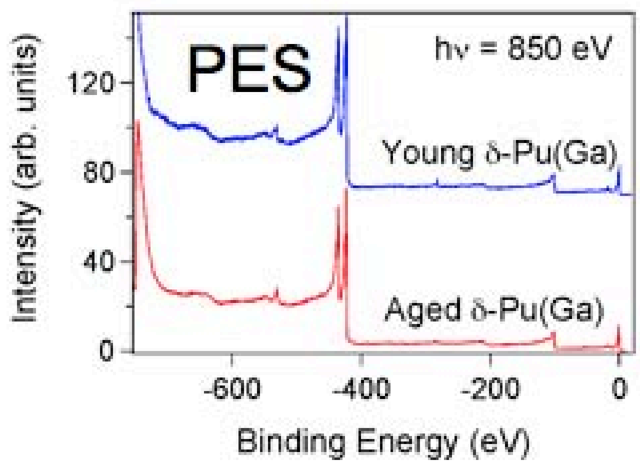
J.G. Tobin et. al., Phys. Rev. B 68, 155109 (2003)

Digression: Almost all spectroscopies of Pu do NOT show strong aging effects

Conventional wisdom – spectroscopies do not show strong, overwhelming, incontrovertible evidence of aging related effects, e.g. XAS[1], PES[1], and EELS[2]



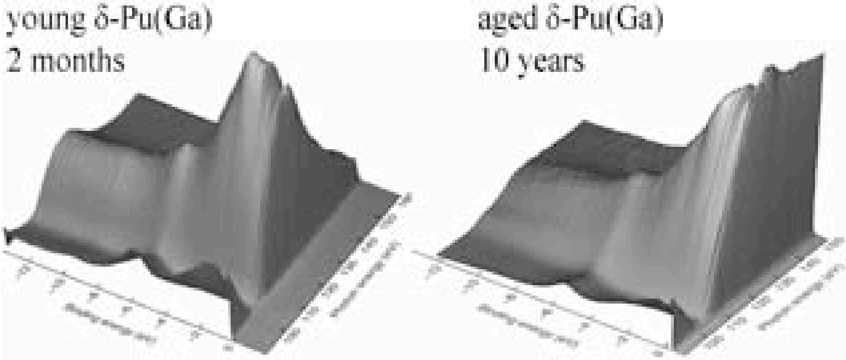
The exception is RESPES!



[1] J.G. Tobin et al., Phys. Rev. B (2003)

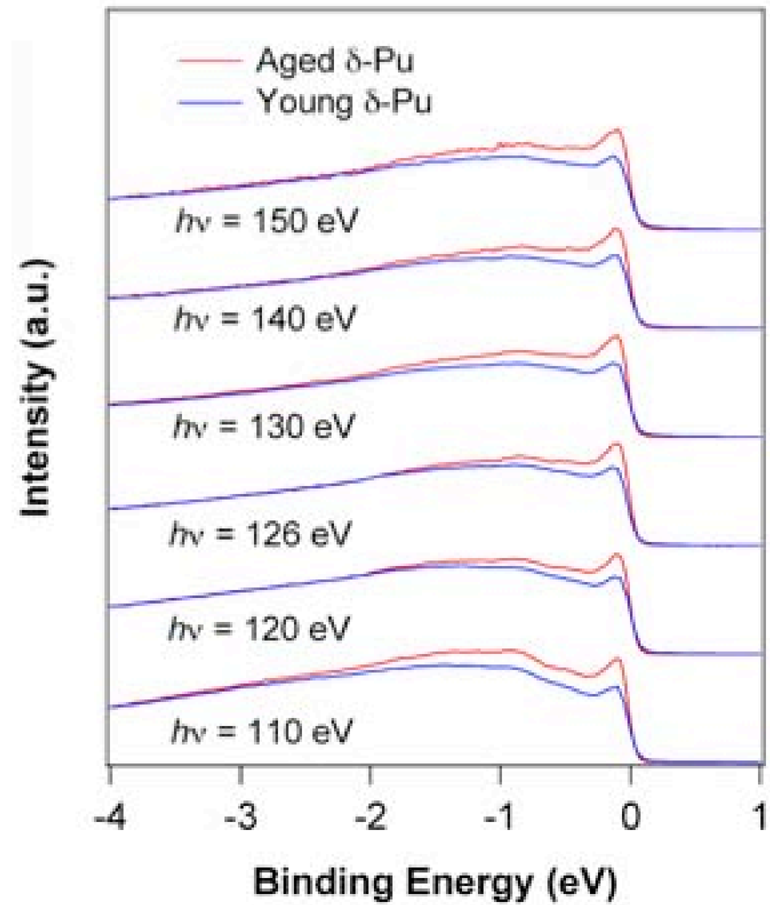
[2] K.T. Moore et al., Phys. Rev. B (2006)

The RESPES effect is amplified in aged δ-Pu(Ga)

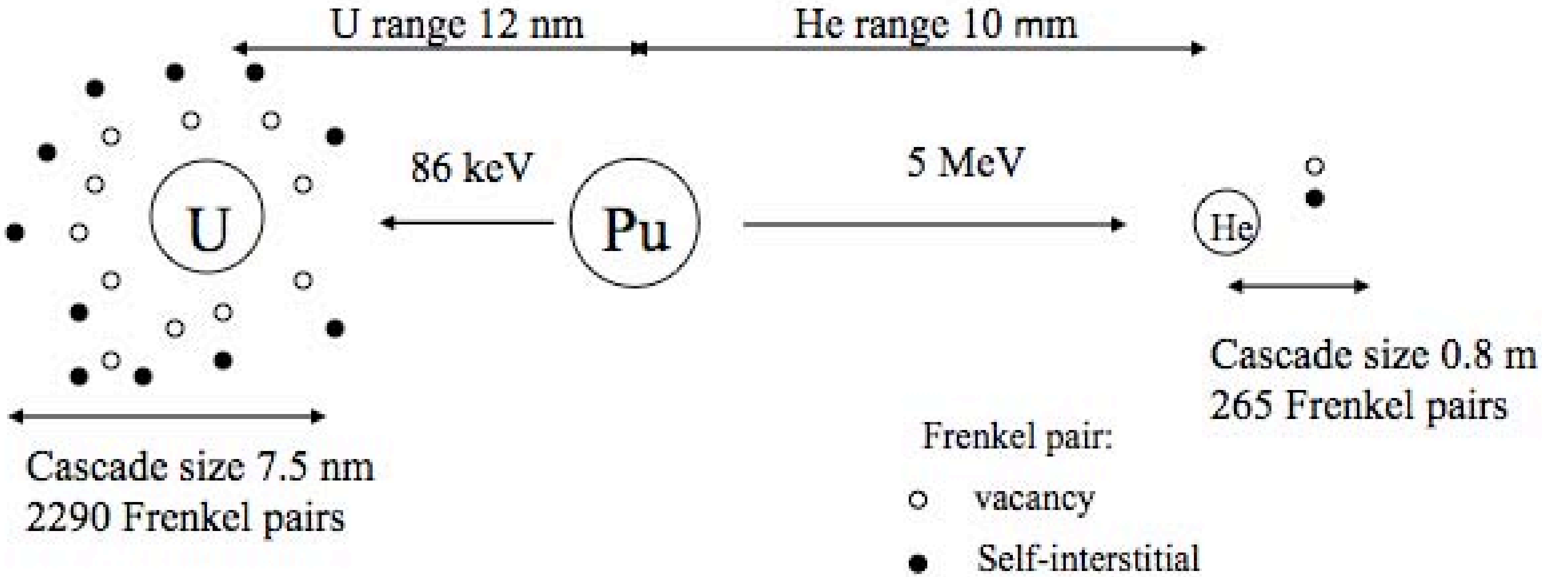


Alternate normalization approaches are used to compare individual spectra at specific photon energies.

There is a consistent amplification of the intensity in the aged sample, on the scale of 30% or so at the Fermi Energy



Digression: Radiation Effects in Plutonium



- **Plutonium decays to uranium atom by alpha (helium nucleus) emission**
- **Both alpha and U atom produce displacement damage**
- **Most of the damage results from the U nucleus**
- **Defects resulting from the residual lattice damage can affect Pu properties**

W.G. Wolfer, Los Alamos Science, 26, 274 (2000)

Digression: Changes in RESPES Across the Nonmetal to Metal Transition in $La_{0.65}Ca_{0.35}MnO_3$

- The photoemission valence band spectra of $La_{0.65}Ca_{0.35}MnO_3$, acquired with photon energies on resonance (55 eV) and off resonance (47 eV), in both the metallic and nonmetallic states.
- The difference curves between the resonant and nonresonant conditions show the resonant enhancement is greater in the nonmetallic or localized state.
- Electron localization or screening effect can be probed directly through RESPES

D.N McIlroy et al., Physics Letters A 207, 367 (1995)

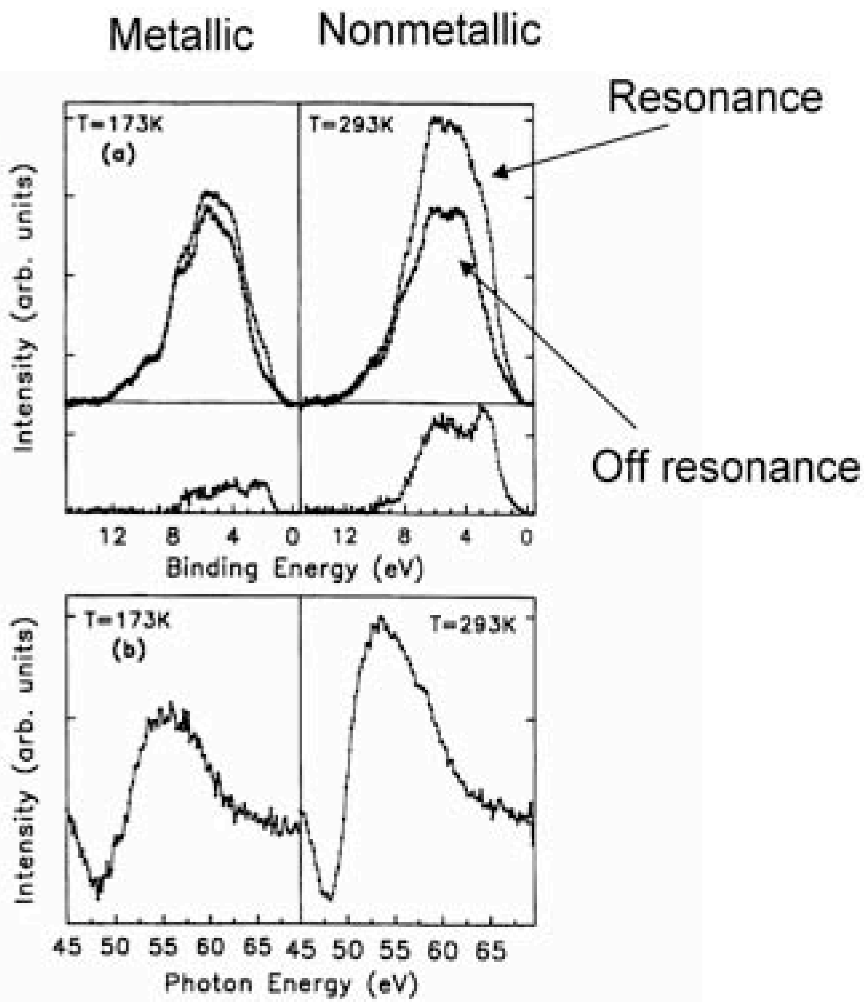
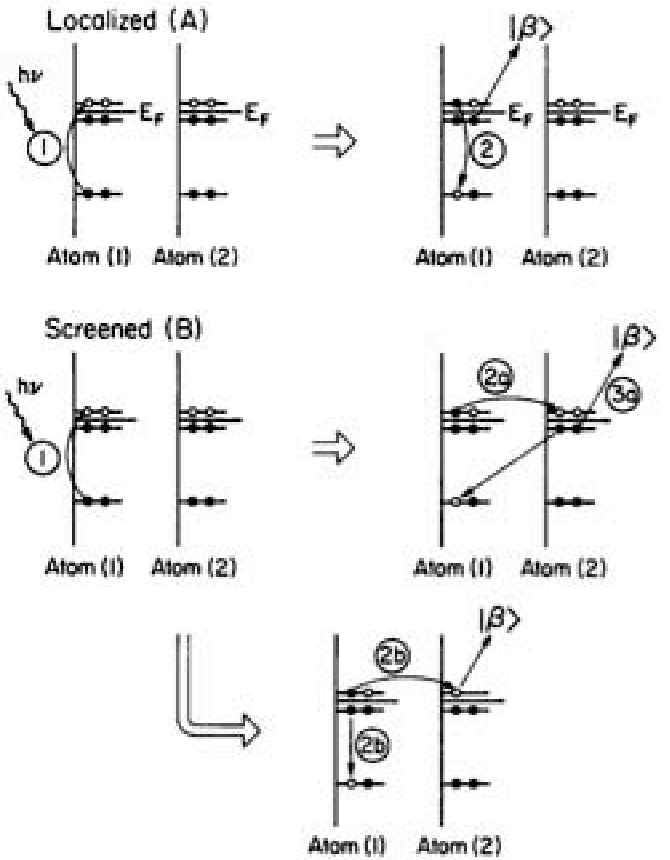


Fig. 3. (a) Valence band spectra of $La_{0.65}Ca_{0.35}MnO_3$ acquired with photon energies of 55 eV (●) and 47 eV (○). The difference curves for the two spectra acquired with different photon energies, but at the same temperature, are displayed below the respective valence spectra. (b) Constant initial state spectra of $La_{0.65}Ca_{0.35}MnO_3$, where the initial state is at a binding energy of 2.7 eV.

Our Interpretation: A Schematic Representation of the RESPES Process for Localized and Screened Decay Cases

- In the localized situation (A), the decay process is limited to one atom
  - only one possible decay process
- With increasing screening (B), extra-atomic interaction can occur
  - additional channels for decay
- In the increased screening case (B), the extra atomic decay channels help to partially quench the RESPES signal
- Aging ---> Disrupted lattice ---> More Localization ---> More RESPES

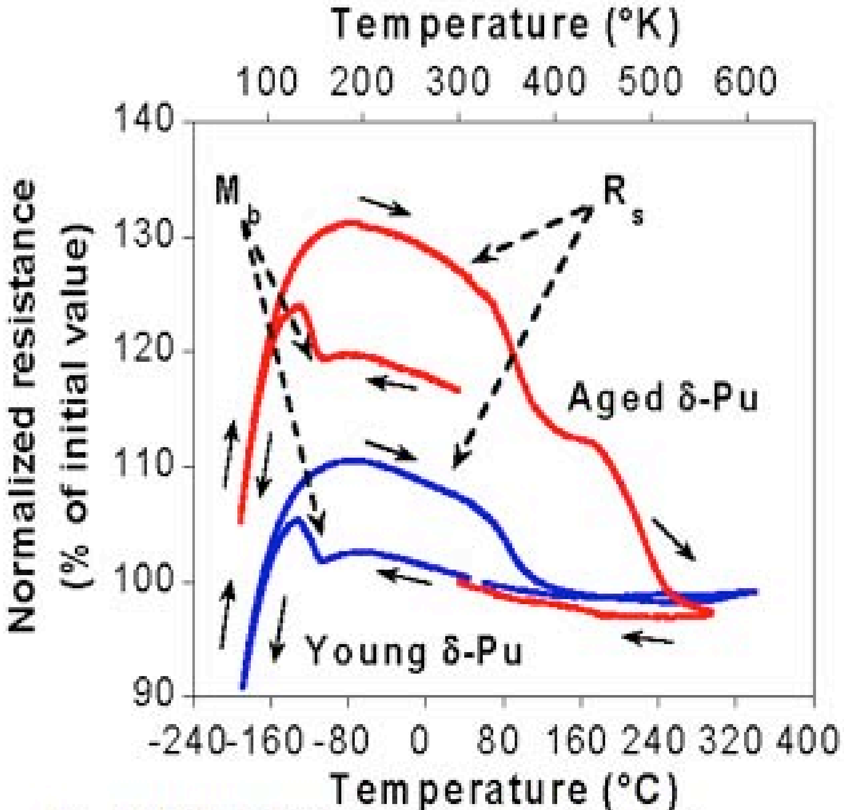


How can we test this hypothesis? The underlying physics of the screening process and conductivity (inverse resistivity) should be the same…

P.A. Dowben, Surface Science Reports 40, 151 (2000)

The effect of annealing upon the residual internal damage in aged δ-Pu(Ga)

- The key effect is at temperatures above 100°C.
- The aged sample exhibits a sharp drop in resistance, while the resistance of the young sample is constant.
- The drop in resistance of the aged sample is a strong indication of the annealing out of the residual internal damage accumulated in the aged sample.
- The more ordered young Pu sample has superior screening, giving rise to RESPES quenching relative to the aged sample.



M_b = Martensite Transition Temperature
R_s = Austenite Start Temperature

B.W. Chung, A.J. Schwartz, B.B. Ebbinghaus, M.J. Fluss, J.J. Haslam, K.J.M. Blobaum, and J.G. Tobin, J. Phys. Soc. Japan 75, No. 5, 054710 (2005).

Partial summary and relation to future plans…

- Resonant Photoelectron Spectroscopy (RESPES) shows sensitivity to aging of plutonium
- The amplified RESPES response in an aged Pu is due to the nanoscale internal damage of the aged sample
  - Analysis based on a screening model developed and tested independently by Peter Dowben
  - The model's application to Pu tested via resistivity and dilatometry measurements
- We now have a spectroscopic signature of aging in Plutonium
- Problem: the likelihood of further RESPES experiments, which require soft x-ray synchrotron radiation and exposed surfaces, is very small.
- Solution: Probe the unoccupied states in house with BIS.

New Approach: BIS or high energy Inverse Photoelectron Spectroscopy

- Bremstrahlung Isochromat Spectroscopy(BIS) of Pu and the other actinides.
- BIS is the high-energy variant of inverse photoelectron spectroscopy (electron in, photon out), which is essentially the time reversal of photoelectron spectroscopy (photon in, electron out).
- From BIS, we would have a direct measure of the conduction band or unoccupied electronic structure.
- Furthermore, by working at higher energies, we will sample preferentially for bulk DOS electronic density, downgrading the impact of surface and band effects, following a philosophy similar to that of Mo et al, PRL 90, 186403 (2003).

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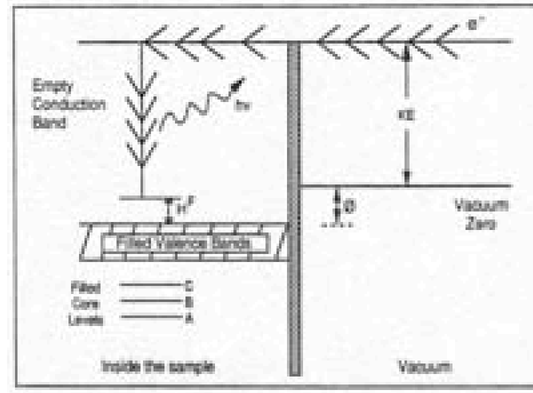
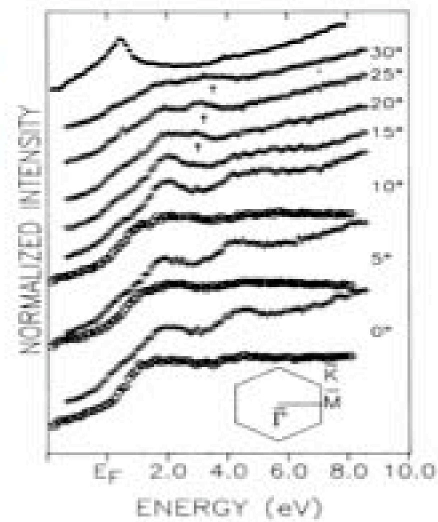


IPES of Ag/Ge(111)
Knapp and Tobin,
PRB 37, 8656 (1988)



O = Ge
\+ = Ag/Ge
● = Ag

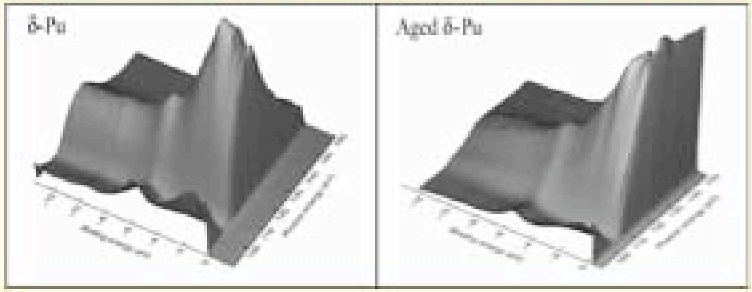
Why bother with BIS?

There are two major reasons

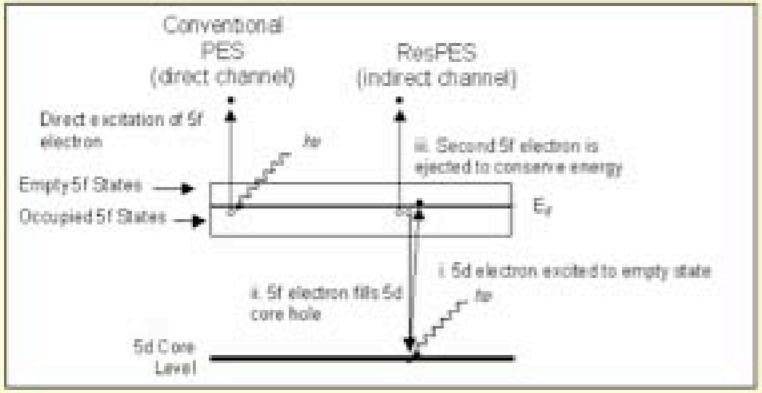
- **First-BIS can directly measure the unoccupied Density of States, but neither EELS nor XAS can do that.**
- **Second-Sensitivity to aging. BIS will be like RESPES, with a sensitivity to the unoccupied electronic structure. So far, the only spectroscopy that demonstrates a sensitivity to aging is RESPES!**

For more about RESPES of Pu, see BW Chung et al, J.Phys.Soc.Japan 75, 5 (2006) and Tobin et al, PRB 68, 155109 (2003).

Spectroscopic Signature of Aging in Pu



Resonant Photoemission shows a strong difference between young and aged Pu samples. RESPES is sensitive to unoccupied electronic structure, just like BIS.

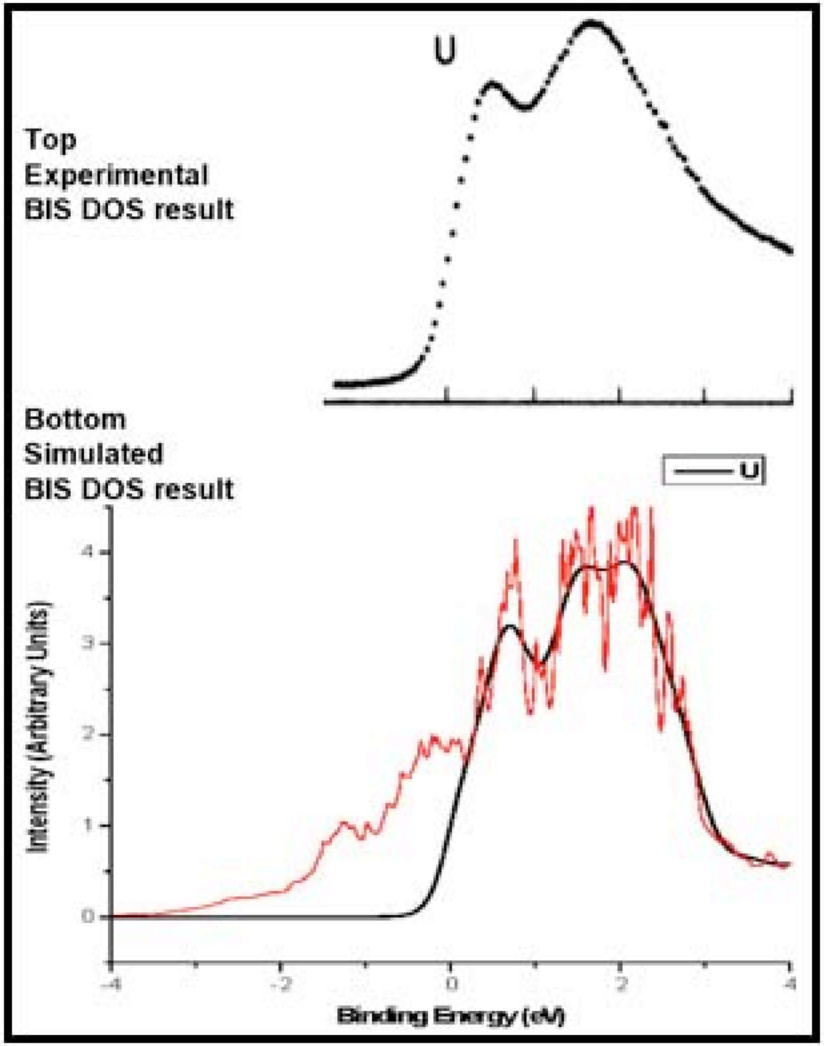


Why bother with BIS? … It works with Uranium!

This is a comparison of an earlier BIS measurement by Baer and Lang [i] of Uranium with a simulated Density of States generated by starting with a calculation by Kutepov (in red), [ii] which is the truncated at the Fermi Energy (only unoccupied states can contribute to BIS) and then smoothed to reflect broadening from the instrumental band-pass (in black).[iii]

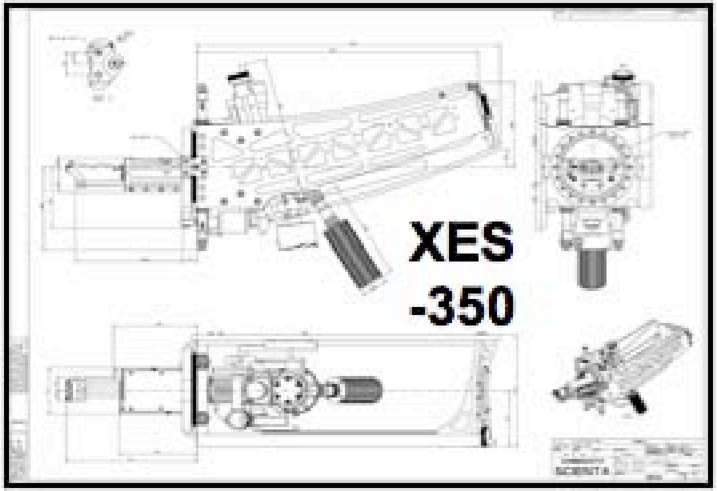
The agreement between experiment and theory is very, very good!

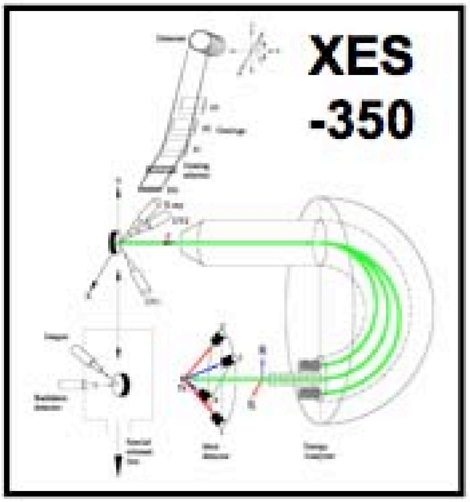
i. Y. Baer and J.K. Lang, Phys. Rev. B 21, 2060 (1980).
ii. J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz,G. van der Laan, and A.L. Kutepov, Phys. Rev. B 72, 085109 (2005).
iii. M.T. Butterfield, J.G. Tobin, N.E. Teslich Jr, R.A. Bliss, M.A. Wall, A.K. McMahan, B.W. Chung, A.J. Schwartz, and A.L. Kutepov, Matl. Res. Soc. Symp. Proc. 893, 95 (2006).



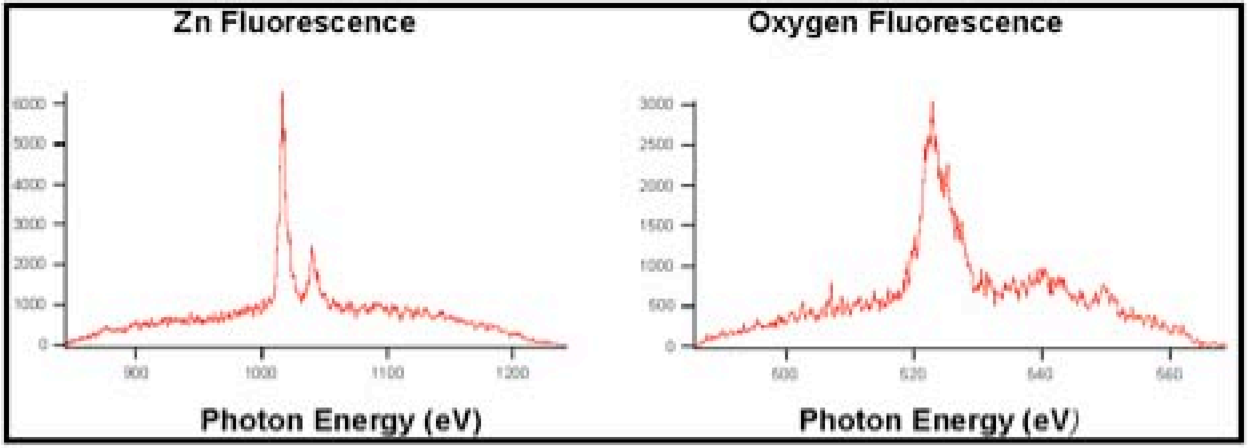
Sung Woo Yu is setting up a BIS capability "in house" at LLNL, along with the Fano Experiment

The XES-350 monochromatized detector is being integrated into the Fano experimental chamber.

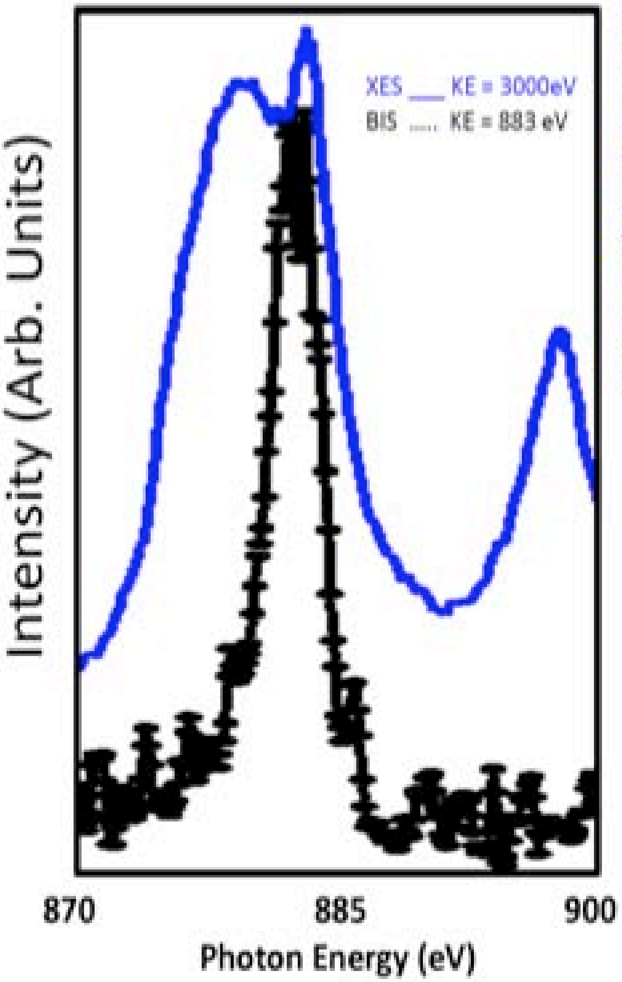




Electron stimulated fluorescence, using an electron excitation beam energy of 3000eV, collected in our lab with the new detector.

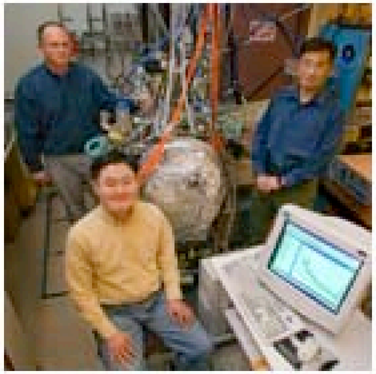


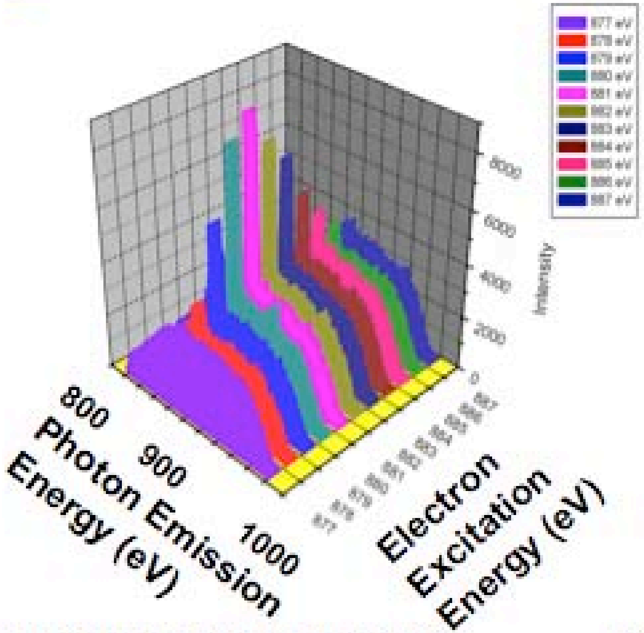
New Bremstrahlung Isochromat Spectroscopy (BIS) Results using CeOxide , from Lab 1226, B235



We are carrying out Inverse Photoelectron Spectroscopy (BIS = IPES) using our XES-350 system. U is next.

To the left:
X-ray Emission Spectroscopy (XES) and Bremstrahlung Isochromat Spectroscopy (BIS) of oxidized Ce. Note the Fermi Edge near 885 eV in the BIS.





To the left, can be seen the resonant behavior near the Ce 3d edge (near 880 eV). These are essentially raw data, showing the output of the XES-350 channel plate.